Supporting Information

Low Temperature Solution-Phase Deposition of SnS Thin Films

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Experimental Details

General considerations. Tin(II) sulfide (Aldrich, 99.99+%) and europium(III) nitrate hexahydrate (Strem, 99.9+%) were purchased and used without further purification. Both 1,2-ethylenediamine (Fluka, 99.5+%) and 1,2-ethanedithiol (98+%, Alfa Aesar) were distilled prior to use. 1,2-Ethylenediamine (en) was first dried for 3 d with either CaO (~120 g per 500 mL) or CaH_2 (~15–20 g per 1 L); after decanting, en was refluxed over Na until a dark blue color was observed (*ca.* 6.5 h) and was then distilled under N_2(g). 1,2-Ethanedithiol (edt) was dried over 3 Å molecular sieves and then distilled. The dissolution was performed using standard Schlenk techniques under N_2(g) in the absence of H_2O and O_2(g). CAUTION: 1,2-ethanedithiol has a pungent odor and should be handled in a fume hood as with any volatile, flammable organic solvent using appropriate personal protection equipment. The thiol may be quenched in a fume hood by slow addition to a large excess of stirred commercial hypochlorite laundry bleach solution (5.25% sodium hypochlorite); a pH > 6 should be maintained by addition of NaOH, if necessary. After stirring for 24 h, the solution can be treated as aqueous waste.

Dissolution of bulk SnS. A typical dissolution experiment entailed addition under flowing N_2(g) of *ca.* 650 mg of thoroughly ground SnS powder into a three-neck round-bottom flask that had been fitted with a reflux condenser and a stir bar. Distilled en (10 mL) and edt (0.9 mL) were then added. The mixture was lightly heated with a heat gun and was sonicated for a *ca.* 10 min. A heating mantle was then used to further heat the mixture to 50 ˚C for 15 h with stirring.

SnS Recovery and Organic Content Determination. *Thermogravimetric analysis (TGA)* was performed in a TA Instruments Q50 TGA. An alumina pan was used to dry 50 µL of the solution mixture *in situ*. The program entailed heating to 125 ˚C and holding this temperature for 15 min, followed by cooling to 30 ˚C and equilibration. The final analysis step entailed heating the sample to 425 ˚C at 10 ˚C min^{-1}. *FT-IR spectroscopy* was performed with a Bruker Vertex 80v and a ZnSe substrate was used to drop cast the SnS mixture followed by an anneal on a hot plate under flowing N_2(g).

Structural and Optical Characterization. *Powder X-ray diffraction (XRD)* patterns were collected using a Cu Kα radiation source (λ = 1.5406 Å) on a Rigaku Ultima IV diffractometer. The diffraction patterns were recorded between 10˚ and 80˚ at room temperature. *Rietveld Analysis.* Rietveld structural refinements were performed using the GSAS software.[1,2]

Table S1. Structural Parameters of SnS Thin Films Extracted From Rietveld Analysis

a (Å)	11.242(3)
b (Å)	3.9943(11)
c (Å)	4.3102(12)
V (Å^3)	193.54(16)
x_{Sn}	0.12356(8)
y_{Sn}	0.25
z_{Sn}	0.11164(14)
x_S	0.1348(3)
y_S	0.75
z_S	0.5199(4)
U_{Sn} (×100)	1.33(4)
U_S (×100)	1.98
R_w (%)	8.72
χ^2	1.47

The crystal structure of the SnS thin films was refined with the orthorhombic *Pnma* space group. The following parameters were refined: (1) scale factor, (2) background, which was modeled using a shifted Chebyschev polynomial function, (3) peak shape, which was modeled using a modified Thomson−Cox−Hasting pseudo-Voigt function,[3] (4) lattice constants (a, b, and c), (5) fractional atomic coordinates of the tin (x_{Sn}, y_{Sn}, z_{Sn}) and sulfur atoms (x_S, y_S, z_S) constrained by the site symmetry, and (6) isotropic displacement parameter of the tin atom (U_{Sn}). The isotropic displacement parameter of the sulfur atom (U_S) was fixed at 1.5 × U_{Sn}. The R_{wp} and χ^2 indicators were employed to assess the quality of the refined structural models.[4] *Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX)* was used for elemental analysis on a JEOL JSM-7001F scanning-electron microscope; SEM imaging was also performed using this instrument. *X-ray photoelectron spectroscopy (XPS)* was performed using a Kratos Axis Ultra X-ray photoelectron spectrometer with the analyzer lens in hybrid mode. High-resolution scans were performed using a monochromatic aluminum anode with an

operating current of 5 mA and a voltage of 10 kV using a step size of 0.1 eV, a pass energy of 20 eV, and a pressure range between 1-3 × 10^{-8} Torr. Binding energies were corrected to correspond to a C1s peak of 284.6 eV. *Diffuse reflectance UV-Vis-NIR spectroscopy* was performed using the reflectivity mode in a Perkin-Elmer Lambda 950 that was equipped with a 150 mm integrating sphere. The samples were prepared by thoroughly grinding 12 mg of SnS with 400 mg of $BaSO_4$ and using a powder sample holder at the end of the integrating sphere.

Spin-Coating. A solution of 60 mg mL^{-1} was filtered using a 0.45 μm filter as 18 drops were deposited on an FTO/glass substrate (1 × 1 in^2) inside a spin coater under flowing N_2(g). The thin films were spin coated using a Laurell Technologies Corporation WS400Ez-6NPP-LITE single-wafer spin processor at 1250 rpm (3 min) for each layer, at an acceleration of 770 rpm s^{-1} for the first coat and 990 rpm s^{-1} for the second coat. The films were annealed between layers (*ca.* 5 ˚C min^{-1}) on a hot plate from room temperature to 350 ˚C under flowing N_2(g). A final anneal of 500 ˚C in a tube furnace, with flowing N_2(g), was performed to increase the robustness of the films for use in the photoelectrochemical experiments.

Photoelectrochemical Characterization. *Electrode preparation*. FTO slides (Sigma Aldrich) with a conductivity of *ca.* 7 Ω sq^{-1} were cut to dimensions of 2.5 cm × 2.5 cm. Films of SnS were prepared as described above. Slides were then cut to 1 cm × 0.5 cm and a portion of the SnS film was removed via mechanical scraping. Silver paint was used to attach a Sn wire to the cleaned portion of the sample, and Loctite 9460 epoxy was applied over the wire and around the edges of the film to mask these areas from solution. Electrodes were allowed to dry for 24–48 h before use. *Illumination and electrochemistry apparatus.* Photocurrent response measurements of the SnS thin films were performed using a Gamry Reference 600 potentiostat. The glass photoelectrochemical cell contained a Pt mesh counter electrode (100 mesh, 99.9% trace metals basis, Sigma-Aldrich), an SCE reference electrode (CH Instruments), and a SnS thin film on FTO-coated glass as the working electrode. The electrolyte consisted of 0.1 M $Eu(NO_3)_3$(aq) as the redox couple. The solution was purged with N_2(g) via bubbling for 10 min prior to the experiments and the N_2(g) was continuously flowed over the head space during the experiments. Simulated sunlight at 100 mW cm^{-2} intensity of Air Mass 1.5 was provided by a W-halogen ELH-type lamp that had been calibrated using a Si photodiode (Thor Laboratories) that was calibrated relative to a NIST-traceable secondary standard photodetector. Nonaqueous electrochemistry was performed anaerobically in an Ar(g)-filled glovebox. The solution consisted of 0.05 M $Eu(OTf)_3$ (OTf^- = $CF_3SO_3^-$) or 20 mM cobaltocene (Cp_2Co) and 20 mM $[Cp_2Co](PF_6)$ with 1.0 M $LiClO_4$. A $Ag|Ag^+$ reference was purchased from CH Instruments and filled with 10 mM $AgNO_3$ and 1 M $LiClO_4$; all nonaqueous measurements were referenced versus this electrode, which was prepared immediately prior to the electrochemical experiments.

Additional Figures

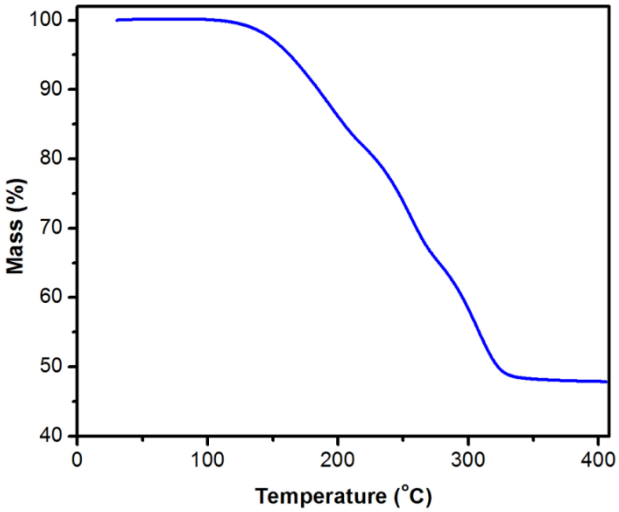

Figure S1. TGA trace showing the decomposition endpoint for a SnS solution in en/edt.

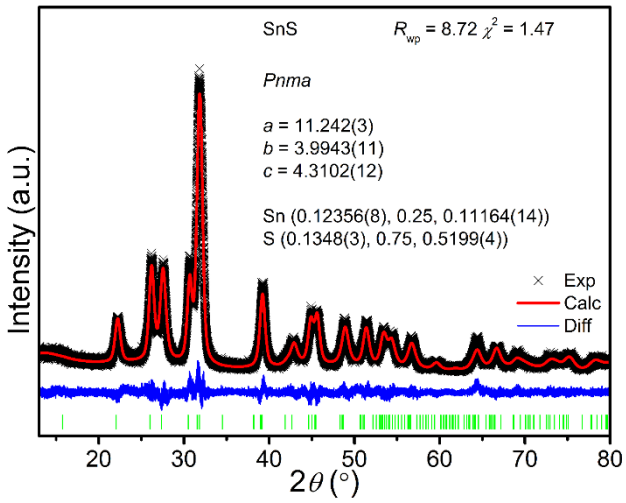

Figure S2. Rietveld analysis of the XRD pattern of SnS thin film. Experimental (×) and calculated (—) patterns are shown along with the difference data (—). Tick marks (|) corresponding to the phase refined are also shown.

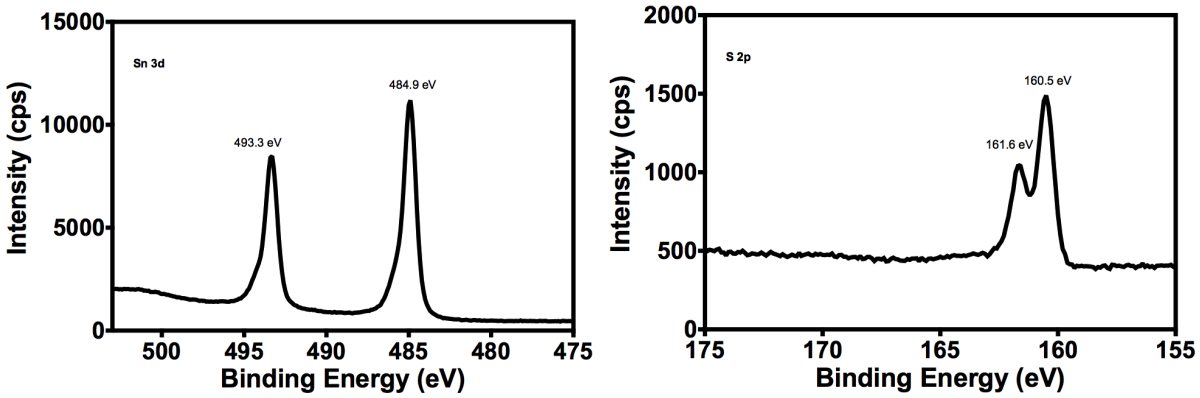

Figure S3. High-resolution XPS spectra of the Sn3d and S2p peaks for the solution-deposited SnS thin films on glass.

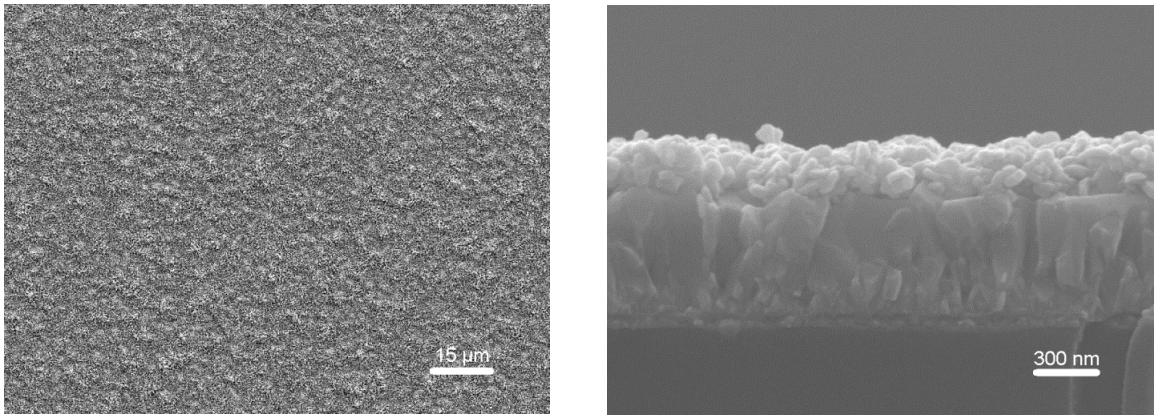

Figure S4. SEM images of SnS films deposited onto FTO using two coats of a 60 mg mL^{-1} SnS ink annealed to 350 ˚C after each layer, with one final anneal to 500 ˚C under $N_2(g)$. A top-down, plane view of the film showed no major cracks or pinholes over a large area (left), and its corresponding cross-section image (right).

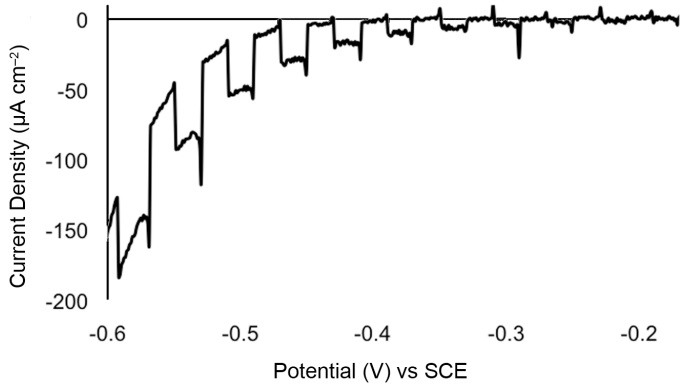

Figure S5. Cyclic voltammogram of *p*-type SnS at 2 mV s^{-1} with chopped simulated 1 Sun illumination every 10 s in contact with 0.1 M $Eu(NO_3)_3$(aq).

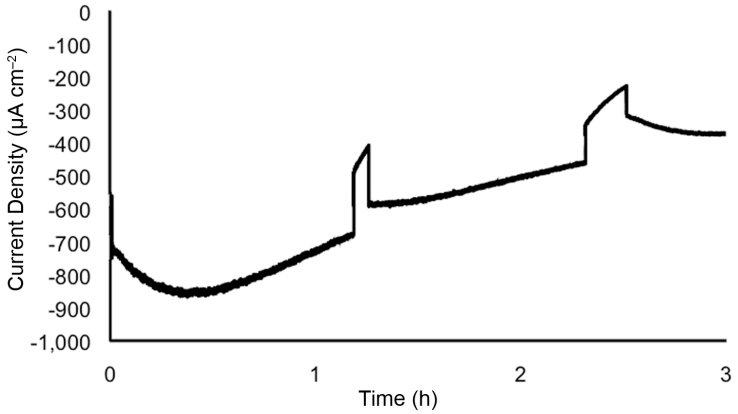

Figure S6. Long-term stability test of *p*-type SnS in 0.1 M $Eu(NO_3)_3$ (aq) at -0.7 V vs SCE. The light was turned off and back on at *ca.* 1 h and 2.5 h where sharp current decreases are observed.

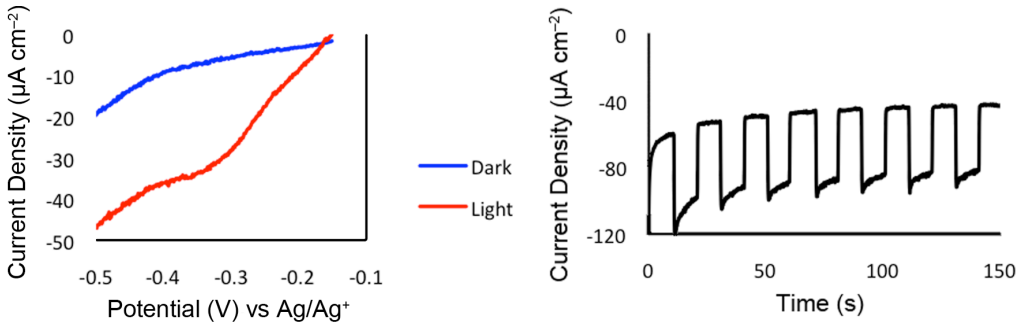

Figure S7. Nonaqueous photoelectrochemistry of *p*-type SnS in contact with 0.05 M $Eu(OTf)_3$ in CH_3CN. (Left) Linear sweep voltammogram from -0.15 to -0.5 V vs $Ag|Ag^+$ in the absence and presence of illumination, respectively. (Right) Chronoamperogram at -0.5 V vs $Ag|Ag^+$ under chopped 1 Sun simulted illumination.

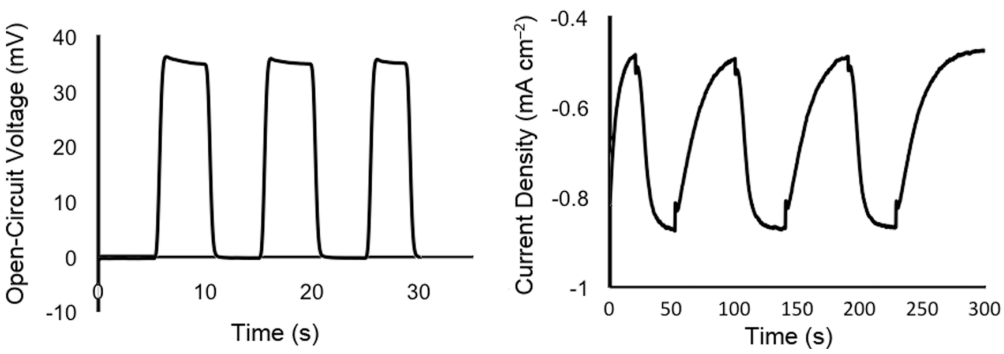

Figure S8. Photoelectrochemical behavior of *p*-type SnS films in contact with $CoCp_2^{+/0}$ in CH_3CN. (Left) Open-circuit voltage under chopped illumination, with *ca.* 35 mV of photovoltage observed, (right) chronoamperometry at -0.2 V vs the Nernstian potential of the solution, under chopped illumination.

Supporting References

1. Larson, A. C.; Von Dreele, R. B. *General Structure Analysis System (GSAS)*; Los Alamos National Laboratory: 2000.

2. Toby, B. H. *J. Appl. Crystallogr.* **2011**, *34*, 210.

3. Thomson, P.; Cox, D. E.; Hastings, J. M. *J. Appl. Crystallogr.* **1987**, *20*, 79.

4. Young, R. A., Oxford University Press: New York, 1993.